SCIENCE FOR CERAMIC PRODUCTION

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ONE-TIME FIRING CERAMIC MIX USING MANUFACTURING WASTE PRODUCTS AS FLUXES

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Compositions of one-time firing ceramic tile have been developed and tested, using as fluxes phosphogypsum and wastes (LiCl) from the production of acetate fiber. The methods of mathematical planning of experiments were used to obtain a system of mathematical equations that describes the dependence of the ceramic tile properties on the content of different components. The computational results are checked.

Key words: facing tile, one-time firing, decrease of energy intensiveness, fluxes, phosphogypsum, wastes from acetate production.

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Ceramic tiles for interior facing are used in construction and remodeling. The main expense items in the manufacturing of such tiles are the materials and fuel costs. Everyone recognizes that the greatest reduction of energy intensiveness can be achieved by adopting a one-time firing technology.

At the present time domestic enterprises use predominately a production cycle with fast two-time firing. Objective difficulties arise in switching to the one-time firing technology, the main one being the lack of mixes developed taking account of the possibilities of the nearest raw materials base. In addition, the deposits of the conventional materials which intensify the sintering process are exhausted or located at considerable distances, as a result of which the raw materials costs are continually increasing. Consequently, the development of a ceramic mix based on local raw materials for one-time firing using fluxes consisting of various manufacturing wastes is a topical problem.

One accessible clayey material for which adequate supplies are available is alkaline nonenriched kaolin from the Ekaterinburg deposit. The uniformity of the composition, high whiteness, and high mechanical properties of the finished product make this material very promising. The mineral composition of alkaline kaolin is as follows (%[3]): 36.1 potassium feldspar, 26.7 kaolinite, 35.1 quartz, and 2.1 other.

However, the elevated content of refractory components makes it necessary to use highly efficient fluxes. The conventional component that intensifies the sintering process is chalk, but when chalk is added, especially with one-time firing, the particulars of its dissociation process must be taken into account [1]. In this connection, priority is given to developing a composition for facing tile, i.e., searching for a flux that intensifies the sintering process with one-time firing.

We have investigated the use of phosphogypsum — a waste from mineral fertilizer production by "EvroKhim – Belorechenskie Minudobreniya" JSC — as a mineralizer. This component is characterized by the following composition: the main substance $CaSO_4 \cdot 2H_2O$ 92% in terms of dry dihydrate, general phosphates 0.9% in terms of P_2O_5, water soluble phosphates 0.2% in terms of P_2O_5, and water soluble fluorine compounds 0.1% in terms of fluorine.

The degree to which phosphogypsum affects the post-firing properties of ceramic tile must be determined first. To this end a series of samples in which chalk was gradually replaced with phosphogypsum was studied.

The mixes were prepared by the slip method. For this, the raw materials, weighed out in accordance with the formu-

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[3] Here and below — content by weight.

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TABLE 1.

Component*	Content, wt.%							
	0.1	1.1	1.2	1.3	1.4	1.5	1.6	1.7
MD chalk (Kopanishchenskoe)	14	12	10	8	6	4	2	–
Phosphogypsum	–	2	4	6	8	10	12	14

* All compositions contained the following (%): 44 VKS-3 clay, 19 "Vesko-Tekhnik" clay, 20 alkaline kaolin, and 3 ground tile scrap.

TABLE 2.

Indicator	Fired ceramic from the mixes							
	0.1	1.1	1.2	1.3	1.4	1.5	1.6	1.7
Shrinkage, %	0.78	0.80	1.05	1.05	1.10	1.77	2.38	3.83
Bending strength, MPa	24.50	24.44	23.73	23.33	21.42	20.83	21.58	24.80
Water absorption, %	15.73	16.07	16.18	16.35	16.48	15.42	14.99	14.20

TABLE 3.

Experiment	Content, wt.%			Shrinkage, %	Bending strength, MPa	Water absorption, %
	phosphogypsum	LiCl*	chalk			
1	6	0.5	6	0.50	23.10	18.70
2	6	0.4	4	0.85	23.00	17.20
3	6	0.3	8	0.89	22.30	17.60
4	8	0.3	8	0.90	2.42	17.00
5	8	0.4	8	0.87	21.42	17.30
6	8	0.5	6	0.55	15.40	19.20
7	10	0.3	6	0.90	20.10	19.60
8	10	0.4	4	1.20	15.20	17.50
9	10	0.5	4	1.00	12.80	17.90
10	4	0.6	6	0.40	13.80	18.48
11	4	0.4	2	0.50	21.42	17.98
12	4	0.2	10	1.65	24.73	14.60
13	8	0.4	10	0.90	23.80	17.20
14	8	0.2	6	1.70	28.20	16.60
15	8	0.6	2	0.70	10.80	20.50
16	12	0.2	6	2.10	23.50	13.30
17	12	0.4	10	0.95	22.50	16.20
18	12	0.6	2	0.65	11.80	24.50
19	2	0.7	6	0.55	10.80	19.40
20	2	0.4	0	0.50	8.80	18.40
21	2	0.1	12	1.40	26.44	13.40
22	8	0.1	6	1.05	29.80	17.10
23	8	0.4	12	1.40	13.20	18.20
24	8	0.7	0	0.60	8.80	22.40
25	14	0.1	6	2.60	29.80	17.10
26	14	0.4	12	2.10	26.90	15.20
27	14	0.7	0	0.60	12.10	18.70

* Over and above 100%.

lation, were wet-ground in porcelain drums in a laboratory roller mill. The residue on a No. 0063 sieve was used to check the fineness and duration of grinding.

The slip was dehydrated in a laboratory desiccator at temperature 100 ± 5°C, after which the molding powder with grain size no greater than 1 mm was prepared. Samples with the dimensions 110 × 55 mm were compacted in a laboratory hydraulic press from molding powder with 5.5% moisture content under pressure 7.5 MPa. The dimensions of a compact were 110 × 55 mm. The firing time with a two-channel production furnace is 30 min with maximum temperature 1100°C. The compositions of the experimental mixes are presented in Table 1.

The samples obtained after firing were subjected to various tests, whose results are presented in Table 2.

Analysis of the experimental determinations of the ceramic mix composition (Table 3) showed that chalk cannot be replaced with phosphogypsum, since in this case the shrinkage far exceeds the admissible amount. However, it should be noted that all samples comply with the standard requirements with regards to strength and, for most samples, water absorption.

The most effective way to decrease the shrinkage of ceramic is to use the waste from the production acetate fiber — LiCl [2], since it effectively intensifies the firing process when added together with material with elevated CaO content. However, because it is difficult to find the content of the individual components the most effective procedure in this case is to use the method of mathematical planning of experiments. On the basis of the particulars of finding the compositions of ceramic mixes Brondon's method is most suitable, since it permits evaluating the effect of each component used.

A series of compositions based on the experiment planning matrix was determined to ascertain the effect of each

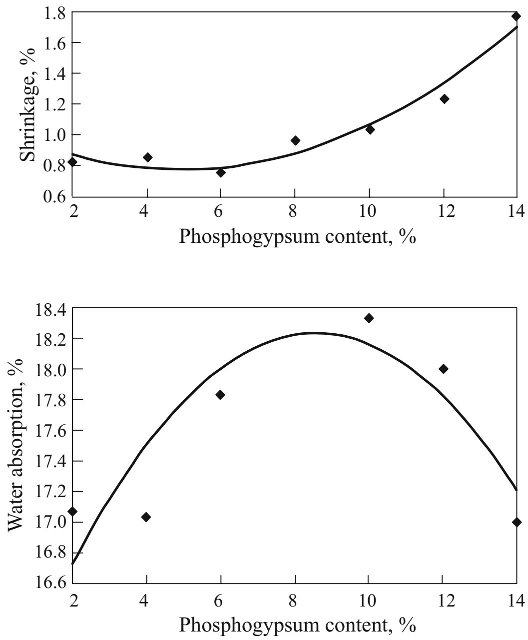

Fig. 1. Shrinkage and water absorption versus the phosphogypsum content.

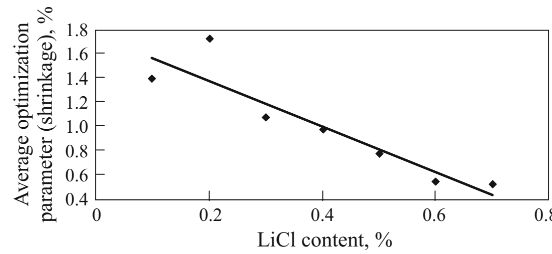

Fig. 2. Shrinkage versus LiCl content.

TABLE 4.

Component*	Content, wt.%		
	1	2	3
MD chalk (Kopanishchenskoe)	4	2	0
Phosphogypsum	8	10	12
LiCl (over and above 100%)	0.28	0.38	0.48

* All compositions contained the following (%): 44 VKS-3 clay, 21 "Vesko-Tekhnik" clay, 20 alkaline kaolin, and 3 ground tile scrap.

TABLE 5.

Indicator	Properties of fired ceramic tile with composition		
	1	2	3
Shrinkage, %	1.05	0.95	0.98
Bending strength, MPa	21.40	17.50	13.86
Water absorption, %	16.62	15.80	17.70

factor on the result when all factors are varied simultaneously.

The following content of the mix components was formulated (%): 44 VKS-3 clay, 20 alkaline kaolin, and 3 ground tile scrap. The content of "Vesko-Tekhnik" clay was varied depending on the amount of chalk and phosphogypsum (see Table 3).

The basic idea of this method of planning an experiment is that the effect of each factor on the result is revealed in experiments where all factors change simultaneously. Plots characterizing the change of the shrinkage and water absorption as a function of the phosphogypsum content were constructed (Fig. 1) on the basis of calculations of the experiment planning matrices.

In addition, curves characterizing the main indicators of fired samples, for example, the shrinkage change versus the LiCl content, were constructed (Fig. 2).

A fit making it possible to describe the plots by means of mathematical equations with adequate reliability was constructed taking account of the dependences obtained. Combining the equations together gave a system that characterizes the main properties of the ceramic as a function of the content of its components:

$$\begin{cases} y_{\text{sh}} = (0.0112x_1^2 - 0.1101x_1 + 1.0414)(-1.8821x_2 + 1.76)(0.0271x_3 + 0.8571); \\ y_\delta = (0.0523x_1^3 - 1.2629x_1^2 + 8.9538x_1 + 1.8971)(-1.6393x_2 + 1.6686)(0.0186x_3 + 0.88); \\ y_w = (-0.0548x_1^2 + 0.545x_1 + 15.5)(0.5107x_2 + 0.8057)(-0.0087x_3 + 1.0511), \end{cases}$$

where the function y_{sh} characterizes the change of shrinkage, the function y_δ characterizes the change of bending strength, the function y_w characterizes the change of water absorption, and x_1, x_2, and x_3 characterize the content (%) of phosphogypsum, LiCl, and chalk, respectively.

Solving the system of equations gives the optimal content of the components as follows (%): 10 phosphogypsum, 0.38 LiCl, 2 chalk, 44 VSK-3 clay, 21 "Vesko-Tekhnik" clay, 20 alkaline kaolin, and 3 ground tile scrap.

According to the calculations this composition should have the following characteristics: shrinkage — 1%, bending strength — 16.73 MPa, and water absorption — 15.98%.

Thus, the computed values of the indicators comply completely with the standards requirements. To check the results in practice three compositions of the ceramic mix were prepared (Table 4). The test results are presented in Table 5.

The results show that the composition 2 is optimal and complies completely with all requirements. Thus, it has been

shown that high-quality ceramic tile can be manufactured with one-time firing using as flux a mixture of phosphogypsum and LiCl, which makes it possible to decrease the production costs.

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